

REMARKS

Claim 7 has been amended and claims 20-31 stand cancelled. Claims 20-29 are newly cancelled as being drawn to non-elected subject matter. No new matter is presented by virtue of the within amendments.

As an initial matter, Applicant affirms its earlier election of Group I, directed to claims 1-19, in response to the Restriction Requirement communicated to the undersigned by phone. Applicant reserves the right to pursue non-elected subject matter (i.e. of claims 20-29) in a divisional application or, alternately, in the present application in the event rejoinder may become available.

Referring now to the more substantive aspects of the Office Action, claim 7 is objected to for allegedly reciting an improper Markush group. Claim 7 has been amended to address this informality. Withdrawal of the rejection is therefore requested.

Claims 1-19 stand rejected under 35 U.S.C. §103(a) over Clark et al. (U.S. Patent 6,306,243) in view of Ederer et al. (WO 01/26885 A1).

The rejection is traversed. Even in combination, the cited references fail to teach or suggest the present invention in any manner sufficient to sustain the rejection.

For instance, the present application discusses Ederer et al. in detail on pages 2-5 of the specification; see in particular page 2, line 22 to page 5, line 12. As outlined on page 5, lines 14-21, it is the object underlying the present invention to provide suitable low-viscosity building materials and bath compositions for the production of three-dimensional models or elements by means of a method, preferably by means of the method described in WO 01/26885 (i.e. Ederer et al.), wherein the building material is deposited in a computer-controlled way onto specific positions of a support layer by layer in form of single droplets, where it is chemically solidified in these positions in the presence of a bath fluid, the outlet port of the dosing device being located above the surface of the bath fluid in order to avoid plugging of the outlet port.

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As discussed in the present application, Ederer et al. do not disclose suitable materials for the bath fluid and the building material. It is merely mentioned that thermoplastic or waxy materials having a viscosity of not more than 20 mPa·s at a temperature of not more than 130°C can be employed, which cool down during deposition and, thus, solidify. However, these kinds of materials exhibit an insufficient thermostability. Thus, Ederer et al. do not disclose suitable building materials fulfilling the requirements of having a low viscosity at the processing temperature, which can be solidified by a chemical reaction or by thermal cross-linking and, subsequently, have a sufficient thermostability and good mechanical properties.

The successful application of the method described by Ederer et al. poses very high demands on building material, bath and the combination thereof. Running systems of this kind were not known at the present application's priority date (at the time when the invention was made).

Clark et al. cannot remedy the deficiencies of Ederer et al. for at least the following reasons. Clark et al. describe "*pH-modified monomer and polymer compositions useful as biomedical and surgical adhesives, sealants, implants and bioactive agent release carriers or matrices. They comprise a monomer or polymer and an effective amount of an acidic or basic pH modifier effective to modify the pH of an immediate in vivo environment of the composition to a pH range at which the polymer biodegrades at a different rate than at physiologic pH. The invention also relates to in vivo applications in which surfaces are joined or treated with such pH modified biocompatible compositions*"; cf. Clark's abstract.

Indeed, the disclosure in Clark et al. relates to a completely different technical field. Therefore, one skilled in the art would not look to Clark et al. as a pertinent reference or as any starting point at all. It is more likely, as outlined above, that the skilled artisan would begin with Ederer et al. However, there is no suggestion whatsoever in Clark et al. that the compositions disclosed therein could be used in the

method of Ederer et al. in order to solve the object underlying the present invention. With knowledge of the present invention, Clark appears to have been identified using some sort of hindsight reconstruction.

Thus, Applicant submits that one skilled in the art would not start from Clark et al. in attempting to arrive at the claimed invention. Rather, the person skilled in the art would start from the method disclosed by Ederer et al. and would try to find suitable materials to be used as building material and bath fluids in order to overcome the disadvantages as discussed on pages 2-5 of the present specification.

The person skilled in the art would clearly not even look to Clark et al. in order to solve the object underlying the present invention. It also is noted that the present claims do not claim 'cyanoacrylate monomers or polymers'. Rather, present claim 1 is directed to a combination of at least one building material and a bath fluid for a method for directly printing elements and models as further specified in the claim. Such a combination is clearly not disclosed or suggested by Clark et al. Indeed, this is expressly acknowledged in the Office Action at page 7, lines 5 and 6.

The person skilled in the art starting from the method as disclosed by Ederer et al., would not have arrived at the claimed combination of the present invention in any manner considered obvious – first, because he would not have combined the teaching of Ederer et al. with that of Clark et al., and second, because no one skilled in the art would have expected that the claimed combination of at least one building material and a bath fluid for a method for directly printing elements and models would work and can actually be used, since its teaching is against the principles of polymer chemistry. That further rebuts any case of *prima facie* obviousness that may be contended.

Moreover, the Office Action acknowledges that Clark et al. disclose that cyanoacrylates are typically polymerized by way of an anionic polymerization. Additionally, according to Clark et al., polymerization of the monomer mixture is accelerated with aqueous solution.

However, to be precise, polymerization of the monomer mixture is accelerated by spraying with a 1% aqueous sodium bicarbonate solution (Examples 1-3, 5, 9-18, 1C-3C, 5C and 9C-18C) or a 1:2:97 triethylamine/methanol/heptane mixture (Examples 4, 6-8, 4C and 6C-8C); cf. column 12, lines 13-18 of Clark et al.

It was not obvious at all from this teaching in Clark et al., i.e. accelerating the reaction of cyanoacrylate monomers by spraying with a 1% aqueous sodium bicarbonate solution, to use in the method of Ederer et al. cyanoacrylate monomers as building material in combination with an aqueous bath fluid in which the initiator is present for at least the following reasons.

- a) According to G. Odian, Principles of Polymerization, 3rd Edition, J. Wiley & Sons, NY 1991, pages 6-9 and 398-425 (copy enclosed), the following is known about polymer chemistry:

"Chain polymerizations require an initiator from which is produced an initiator species R^{\bullet} with a reactive center. The reactive center may be either a free radical, cation, or anion. Polymerization occurs by the propagation of the reactive center by the successive additions of large numbers of monomer molecules in a chain reaction happening, in a matter of a second or so at most, and usually in much shorter times. Monomer can react only with a propagating reactive center, not with the monomer. By far the most common example of chain polymerization is that of vinyl monomers". See page 7 of Odian, second paragraph and reaction formula.

"The growth of the polymer chain ceases when the reactive center is destroyed by one of a number of possible termination reactions". See page 7 of Odian, penultimate paragraph.

Accordingly, a polymer chain is built of one initiator species and a large number of monomer molecules.

- b) The polymerization mechanism disclosed in general with respect to free radical, cationic and anionic polymerization in the "Introduction" on page 7 of Odian is discussed in detail in Chapter 5-3 on pages 398-425 of Odian. As discussed above, anionic polymerization is the polymerization mechanism underlying the polymerization of cyanoacrylates by spraying with a 1% aqueous sodium bicarbonate solution as taught by Clark et al.

"The range of solvents useful for anionic polymerization is limited to aliphatic and aromatic hydrocarbons and ethers". See page 398, third to last line.

"Termination occurs by transfer of a positive fragment, usually a proton, from the solvent or some transfer agent (often deliberately added), although other modes of termination are also known". See page 399, lines 3-5.

Furthermore, as outlined on page 404 of Odian, beginning in line 5: *"Any moisture present terminates propagating carbanions by proton transfer [...]. The hydroxide ion is usually not sufficiently nucleophilic to reinitiate polymerization and the kinetic chain is broken. Water has an especially negative effect on polymerization, since it is an active chain-transfer agent. For example, $C_{tr,S}$ is approximately 10 in the polymerization of styrene at 25°C with sodium naphthalene [Szwarc, 1960], and the presence of even small concentrations of water can greatly limit the polymer molecular weight and polymerization rate. [...]. Living polymers are terminated by the deliberate addition of a chain-transfer agent such as water or alcohol to the reaction system after all of the monomer has reacted".*

Thus, water is a chain-transfer agent and terminates typical anionic polymerizations, since the carbanion as the end-group of the propagating polymer chain reacts with a proton of the water by formation of a OH^- ion and the carbanion is transferred in a non-reactive end-group. Accordingly, growth of the polymeric chain is stopped. Since the OH^- ion is not sufficiently nucleophilic to reinitiate polymerization not only the real chain is broken, however, also the kinetic chain. Thus, the polymerization is stopped in total if water is present as an impurity.

- c) With respect to cyanoacrylates the situation is a little bit different. *"A monomer, such as methyl- α -cyanoacrylate, with two electron-withdrawing substituents can be polymerized with very mild nucleophiles [...]. Polymerization probably involves initiation by water (or OH^- from water) [...]"*. See page 400 of Odian, last five lines of the penultimate paragraph.

The consequences of this fact are as follows:

- i) Either water is not the initiator, however, OH^- is the initiator.
- In such a case, water is a classical chain-transfer agent. This means that the carbanion at the end of a growing polymer chain reacts with water, thus, resulting in a non-reactive end-group. However, an OH^- ion is built which can initiate a new chain. In such a case, the length of the chain is inverse proportional to the formula $C_{tr} [\text{H}_2\text{O}]/[\text{M}]$. C_{tr} is the chain-transfer constant for water and $[\text{H}_2\text{O}]$ and $[\text{M}]$ are the concentrations of water and monomer, respectively. C_{tr} is about ten (see Odian, page 404, line 9-10). Thus, if water is present in a large excess, such as in the combination according to claim 1 of the present invention, comprising a bath fluid consisting of an aqueous solution containing an initiator, and a small drop of cyanoacrylate is introduced into the aqueous bath fluid, the term $C_{tr} [\text{H}_2\text{O}]/[\text{M}] \gg 1$. Thus, the

degree of polymerization is $\ll 1$, such that according to the teaching in textbooks of this field of technology no polymer can be formed.

- ii) In the other case, if water itself acts as an initiator (i.e. $[H_2O]=[I]$), the degree of polymerization of a non-living polymerization is inverse proportional to the root of $[I]$ (concentration of the initiator), and in case of a living polymerization, it is inverse proportional to $[I]$. According to Odian (see page 410), practically all analysed anionic polymerization reactions are living polymerizations, with the only exception being the polymerization in liquid ammonia initiated by KNH_2 . Thus, also in such a case, according to textbook knowledge, it is not possible to obtain a polymer when a small drop of monomer is poured into a large excess of water.

Thus, in the presence of larger amounts of water no polymer can be formed in a typical anionic polymerization reaction.

- d) Accordingly, the teaching of the present invention involves an inventive step, since the findings of the present inventors are contrary to textbook knowledge and it was surprising that it is possible, according to the teaching of the present invention, to obtain a solid material by polymerization of a building material being dropped into a bath fluid consisting of an aqueous solution containing an initiator.
- e) Applicant firmly submits that for at least the reasons given above, according to the teaching by Clark et al., the aqueous sodium bicarbonate solution is sprayed on the monomer mixture, because according to textbook knowledge, the person skilled in the art would not have considered it to be possible to obtain a polymer having a sufficient degree of polymerization, if too much water would have come into contact with

the cyanoacrylate (e.g. by dropping the cyanoacrylate into an aqueous solution, as according to the teaching of the present invention).

In summary, rather than starting from Clark et al., the person skilled in the art would have started from the teaching of Ederer et al. (as discussed in the present specification) in an effort to solve the object underlying the present invention. However, the person skilled in the art would not have taken the teaching of Clark et al. into consideration, because Clark et al. does not even relate to the same technical field and does not relate to the object underlying the present invention. Finally, even assuming for argument's sake that the person skilled in the art would have taken Clark et al. into consideration, he would not have arrived at the claimed subject-matter in an obvious manner, since Clark et al. only disclose spraying a 1% aqueous sodium bicarbonate solution on the monomer mixture to accelerate the polymerization, rather than providing a combination of at least one building material containing a cyanoacrylate and a bath fluid consisting of an aqueous solution containing an initiator, suitable to be used in the method disclosed by Ederer et al. The person skilled in the art would not have assumed or had any reason to expect that such a combination would work. With due respect given to general textbook knowledge, the person skilled in the art would not have tried such a combination with any reasonable expectation of success. Therefore, the claimed-subject-matter involves an inventive step and is not obvious in view of the cited art.

For at least the foregoing reasons, the §103 rejection should be withdrawn. To establish a *prima facie* case of obviousness, three basic criteria must be met: (1) there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings; (2) there must be a reasonable expectation of success; and (3) the prior art reference(s) must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art, and not based

on applicant's disclosure. *In re Vaeck*, 947 F.2d 488, 20 USPQ2d 1438 (Fed. Cir. 1991). See MPEP § 2143.

In the present case, there is no suggestion or motivation, either in the reference itself or in the knowledge generally available to one of ordinary skill in the art, to modify or combine the cited references to arrive at the presently-claimed invention, nor is there any reasonable expectation of success. A *prima facie* case of obviousness therefore cannot be established, and the rejection must be withdrawn.

In view of the above amendments and remarks, Applicant believes the pending application is in condition for immediate allowance.

Dated: October 16, 2006

Respectfully submitted,

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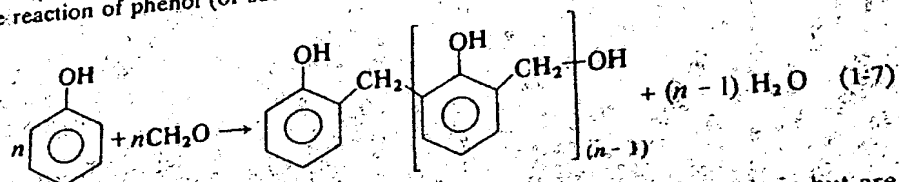
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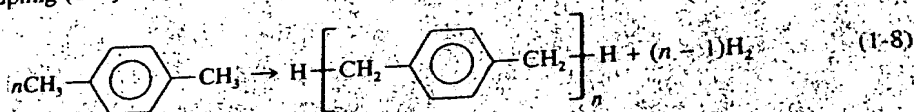
APPENDIX

An excerpt follows from Principles of Polymerization, 3rd edition, J. Wiley & Sons, NY 1991: pages 6-9 and 398 and 425.

polymers by Carothers's classification will also be so defined by a consideration of the polymer chain structure. Some condensation polymers do not contain functional groups in the polymer chain. An example is the phenol-formaldehyde polymers produced by the reaction of phenol (or substituted phenols) with formaldehyde



These polymers do not contain a functional group within the polymer chain but are classified as condensation polymers, since water is split out during the polymerization process. Another example is poly(*p*-xylylene), which is produced by the oxidative coupling (dehydrogenation) of *p*-xylene:

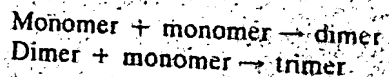


In summary, a polymer is classified as a condensation polymer if its synthesis involves the elimination of small molecules, or it contains functional groups as part of the polymer chain, or its repeating unit lacks certain atoms that are present in the (hypothetical) monomer to which it can be degraded. If a polymer does not fulfill any of these requirements, it is classified as an addition polymer.

1-1b Polymerization Mechanism

In addition to the structural and compositional differences between polymers, Flory [1953] stressed the very significant difference in the mechanism by which polymer molecules are built up. Polymerizations are classified into step and chain polymerizations based on the polymerization mechanism. (The terms *step-reaction polymerization* and *chain-reaction polymerization* are also used instead of step polymerization and chain polymerization, respectively.) Step polymers are, then, those produced by step polymerization and chain polymers, those produced by chain polymerization. The characteristics of the two polymerizations are considerably different. The two reactions differ basically in terms of the time-scale of various reaction events. More specifically, step and chain polymerizations differ in the length of time required for the complete growth of full-sized polymer molecules.

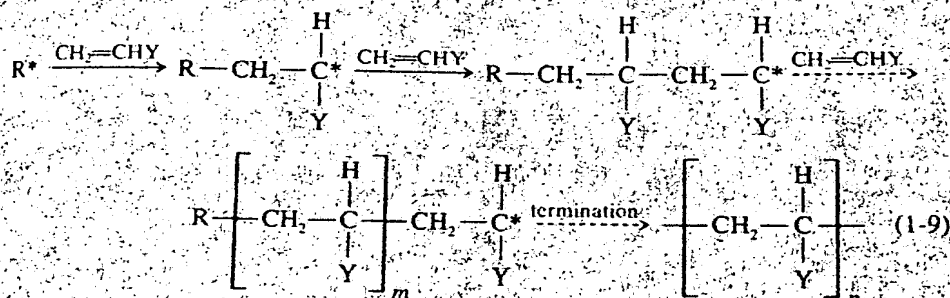
Step polymerizations proceed by the stepwise reaction between the functional groups of reactants as in reactions such as those described by Eqs. 1-1 through 1-3 and Eqs. 1-6 through 1-8. The size of the polymer molecules increases at a relatively slow rate in such polymerizations. One proceeds slowly from monomer to dimer, trimer, tetramer, pentamer, and so on:



Dimer + dimer \rightarrow tetramer
 Trimer + monomer \rightarrow tetramer
 Trimer + dimer \rightarrow pentamer
 Trimer + trimer \rightarrow hexamer
 Tetramer + monomer \rightarrow pentamer
 Tetramer + dimer \rightarrow hexamer
 Tetramer + trimer \rightarrow heptamer
 Tetramer + tetramer \rightarrow octamer
 etc.

until eventually large polymer molecules containing large numbers of monomer molecules have been formed. Any two molecular species can react with each other throughout the course of the polymerization. The situation is quite different in chain polymerizations where full-sized polymer molecules are produced almost immediately after the start of the reaction.

Chain polymerizations require an initiator from which is produced an initiator species R^* with a reactive center. The reactive center may be either a free radical, cation, or anion. Polymerization occurs by the propagation of the reactive center by the successive additions of large numbers of monomer molecules in a chain reaction happening in a matter of a second or so at most, and usually in much shorter times. Monomer can react only with the propagating reactive center, not with monomer. By far the most common example of chain polymerization is that of vinyl monomers. The process can be depicted as:



The growth of the polymer chain ceases when the reactive center is destroyed by one of a number of possible termination reactions.

One should not infer from the above discussion that chain polymerizations are faster than step polymerizations. The net rate at which monomer molecules disappear (i.e., the rate of polymerization) in step polymerization can be as great as or greater than that in chain polymerization. The difference between the two processes lies simply in the time required for the growth of each polymer molecule compared to the time required to achieve high conversions. Thus if we start out a chain polymerization and a step polymerization side by side we may observe a variety of situations with regard to their relative rates of polymerization. However, the molecular weights of the polymers produced at any time after the start of the reactions will always be very characteristically different for the two polymerizations. If the two polymerizations are stopped at 0.1% conversion, 1% conversion, 10% conversion, 45% conversion, 90% conversion, and so on, one will always observe the same behavior. The chain poly-

8 INTRODUCTION

merization will show the presence of high-molecular-weight polymer molecules at all percents of conversion. There are no intermediate sized molecules in the reaction mixture—only monomer, high-polymer, and initiator species. The only change that occurs with conversion (i.e., reaction time) is the continuous increase in the number of polymer molecules (Fig. 1-1A). Polymer size is generally independent of percent conversion, although the amount of polymer certainly depends on it. On the other hand, high-molecular-weight polymer is obtained in step polymerizations only near the very end of the reaction (>98% conversion) (Fig. 1-1B). Thus both polymer size and the amount of polymer are dependent on conversion in step polymerization.

The classification of polymers according to polymerization mechanism, like that by structure and composition, is not without its ambiguities. Certain polymerizations

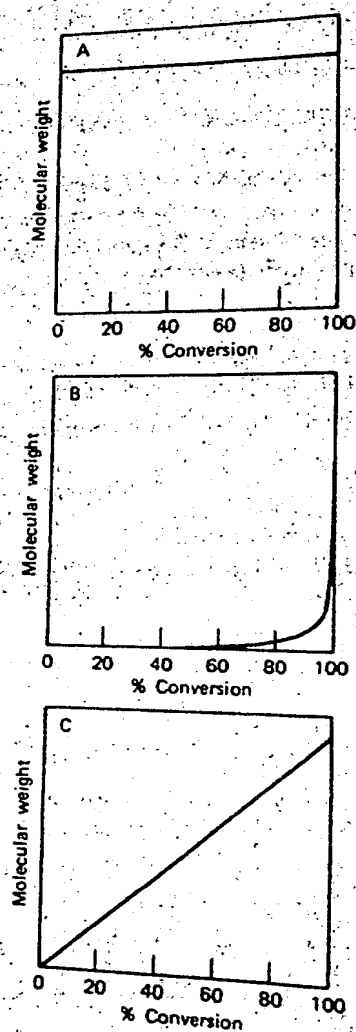
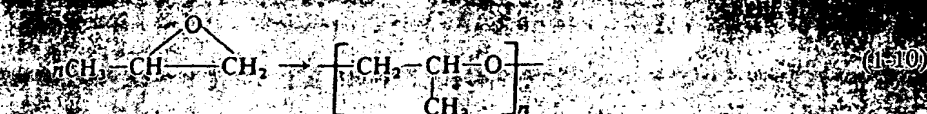


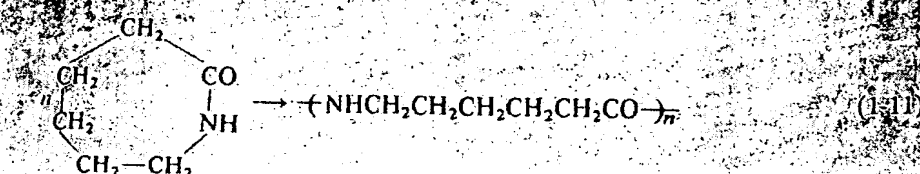
Fig. 1-1 Variation of molecular weight with conversion: A, chain polymerization; B, step polymerization; C, nonterminating ionic chain polymerization and protein synthesis.

show a linear increase of molecular weight with conversion (Fig. 1-1C) when the polymerization mechanism departs from the normal step or chain pathway. This is observed in certain ionic chain polymerizations, which involve a fast initiation process coupled with the absence of reactions that terminate the propagating reactive centers. Biological syntheses of proteins also show the behavior described by Fig. 1-1C because the various monomer molecules are directed to react in a very specific manner by an enzymatically controlled process.

The ring-opening polymerizations of cyclic monomers such as propylene oxide,



or ϵ -caprolactam,



proceed either by step or chain mechanisms, depending on the particular monomer reaction conditions, and initiator employed. The polymer obtained is the same regardless of the polymerization mechanism. Such polymerizations point out very clearly that one must distinguish between the classification of the polymerization mechanism and that of the polymer structure. The two classifications cannot always be used interchangeably. Polymers such as the polyethers and polyamides produced in Eqs. 1-10 and 1-11, as well as those from other cyclic monomers, must be separately classified as to polymerization mechanism and polymer structure. These polymers are structurally classified as condensation polymers, since they contain functional groups (e.g., ether, amide) in the polymer chain. They, like the polyurethanes, are not classified as addition polymers by the use of Carothers's original classification. The situation is even more complicated for a polymer such as that obtained from ϵ -caprolactam. The exact same polymer can be obtained by the step polymerization of the linear monomer ϵ -aminocaproic acid. It should suffice at this point to stress that the terms condensation and step polymer or polymerization are not synonymous nor are the terms addition and chain polymer or polymerization, even though these terms are often used interchangeably. The classification of polymers based only on polymer structure or only on polymerization mechanism is often an oversimplification that leads to ambiguity and error. Both structure and mechanism are usually needed in order to clearly classify a polymer.

1-2 NOMENCLATURE OF POLYMERS

Polymer nomenclature in general leaves much to be desired. A standard nomenclature system based on chemical structure as is used for small inorganic and organic compounds is most desirable. Unfortunately, the naming of polymers has not proceeded in a systematic manner until relatively recently. It is not at all unusual for a polymer

The isoprene incorporates double bonds into the polymer chains, which makes subsequent vulcanization (crosslinking) possible (Sec. 9-2b). The amount of isoprene is in the range of 0.5–2.5% of the amount of isobutylene, the exact amount depending on the extent of crosslinking that is desired. Molecular weights of at least 200,000 are needed to obtain products that are not tacky. Control of molecular weight is achieved by working at the lower reaction temperatures and regulating the amounts of transfer and terminating agents present. Butyl rubber, unlike natural rubber, does not crystallize on cooling and hence remains flexible down to -50°C . The low degree of unsaturation imparts good resistance to aging, moisture, chemicals, and ozone. The low gas permeability of butyl rubber makes it well suited for innertubes for tires (which are still used in most nonpassenger automobile tires). The high-damping behavior of butyl rubber makes it well suited for engine and auto-body mounts. Other uses include electrical cable insulation, protective gloves, chemical tank liners, and pharmaceutical stoppers.

5-2i-2 Other Products

Hydrocarbon resins comprise a range of low-molecular-weight products ($M_n < 3000$) used as adhesives, hot-melt coatings, tackifying agents, inks, and additives in rubber [Kennedy and Marechal, 1982]. These include products based on monomers derived from petroleum as well as plant sources. The petroleum-derived products include polymers produced from various alkenes, isoprene, piperylene, styrene, α -methylstyrene, vinyltoluene, and dicyclopentadiene. The plant-derived products include *polyterpenes* obtained by the polymerization of dipentene, α -pinene, and β -pinene. Low-molecular-weight coumarone-indene polymers, referred to as *coal-tar resins*, are used in surface coatings and floor tiles.

The polymerization of alkyl vinyl ethers is of some commercial importance. The homopolymers, which can be obtained only by cationic polymerization, are useful as plasticizers of other polymers, adhesives, and coatings. (The copolymerization of vinyl ethers with acrylates, vinyl acetate, maleic anhydride, and other monomers is achieved by radical polymerization but not the homopolymerizations of alkyl vinyl ethers.)

5-3 ANIONIC POLYMERIZATION OF THE CARBON-CARBON DOUBLE BOND

Anionic chain polymerizations show many of the same characteristics as cationic polymerizations, although there are some distinct differences. The propagating species are anionic ion pairs and free ions with relative concentrations that depend on the reaction media as in cationic polymerization. Unlike cationic polymerization, there is a large difference in the reactivities of ion pairs and free ions in anionic polymerization. Although anionic polymerizations generally proceed rapidly at low temperatures, they are seldom as temperature-sensitive as cationic polymerizations. Further, most anionic polymerizations possess positive E_a values and proceed well at and somewhat above ambient temperatures. Many anionic polymerizations are easier to understand since the identities of the initiating species and counterions are much better established. The range of solvents useful for anionic polymerization is limited to aliphatic and aromatic hydrocarbons and ethers. Halogenated solvents, suitable for cationic polymerization, cannot be used for anionic polymerization because of their facile nucleophilic

substitution reactions with carbanions. Other polar solvents such as esters and ketones are also excluded as a result of reaction with carbanions.

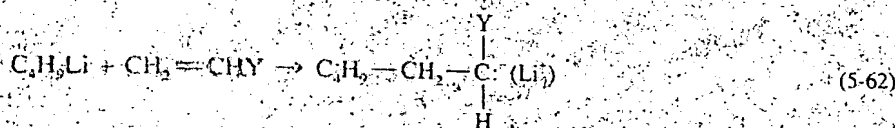
Termination occurs by transfer of a positive fragment, usually a proton, from the solvent or some transfer agent (often deliberately added), although other modes of termination are also known. Many anionic polymerizations are living polymerizations when the reaction components are appropriately chosen.

5-3a Initiation

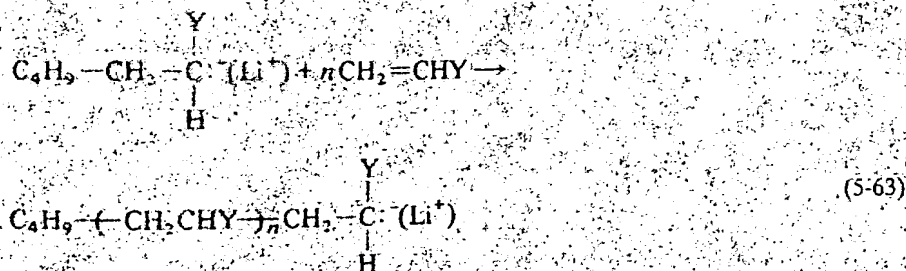
5-3a-1 Nucleophilic Initiators

A variety of basic (nucleophilic) initiators have been used to initiate anionic polymerization [Bywater, 1975, 1976, 1985; Fontanille, 1989; Morton, 1983; Morton and Fetters, 1977; Richards, 1979; Szwarc, 1983; Young et al., 1984]. These include covalent or ionic metal amides such as NaNH_2 and $\text{LiN}(\text{C}_2\text{H}_5)_2$, alkoxides, hydroxides, OMgBr , phosphines, amines, and organometallic compounds such as $n\text{-C}_4\text{H}_9\text{Li}$ and a neutral (B^-) or negative (B^{--}) species.

Alkyl lithium compounds are probably the most useful of these initiators, employed commercially in the polymerizations of 1,3-butadiene and isoprene. Initiation proceeds by addition of the metal alkyl to monomer



followed by propagation

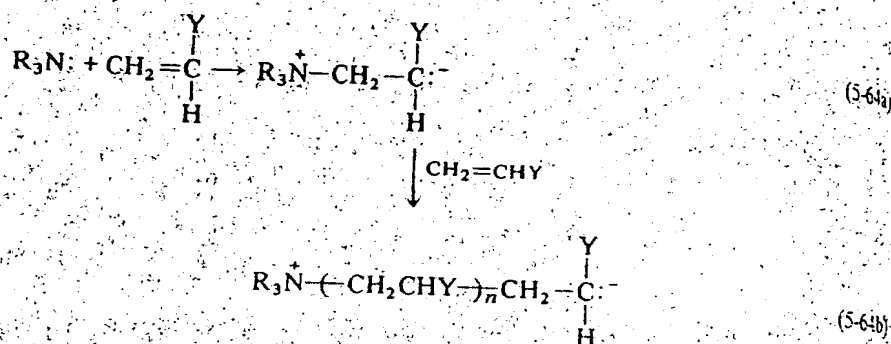


The extensive use of alkyl lithium initiators is due to their solubility in hydrocarbon solvents. Alkyls or aryls of the heavier alkali metals are poorly soluble in hydrocarbons, as a consequence of their more ionic nature. The heavier alkali metal compounds, as well as alkyl lithiums, are soluble in more polar solvents such as ethers. The use of most of the alkali metal compounds in ether solvents, especially the more ionic ones, is somewhat limited by their reactivity toward ethers. The problem is overcome by working below ambient temperatures and/or using less reactive (i.e., resonance-stabilized) anions as in benzylpotassium, cumylcesium, and diphenylmethyl lithium.

Alkyl derivatives of the alkaline-earth metals have also been used to initiate anionic polymerization. Organomagnesium compounds are considerably less active than organolithiums as a result of the much less polarized metal-carbon bond. They can

only initiate polymerization of monomers more reactive than styrene and 1,3-dienes such as 2- and 4-vinylpyridines, and acrylic and methacrylic esters. Organostrontium and organobarium compounds, possessing more polar metal-carbon bonds, are able to polymerize styrene and 1,3-dienes as well as the more reactive monomers.

In the relatively few anionic polymerizations initiated by neutral nucleophiles such as an amine or phosphine

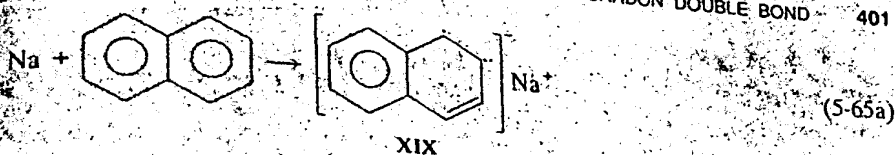


the proposed propagating species is a *zwitterion* [Cronin and Pepper, 1988; Eromosele et al., 1989; Pepper and Ryan, 1983]. The zwitterion propagating species has the glaring deficiency of requiring increasing charge separation as propagation proceeds. Stabilization of zwitterion species may involve the positive end of one zwitterion propagating chain acting as the counterion of the carbanion end of another zwitterion propagating chain. The need for a zwitterion propagating species is avoided if initiation is proposed as occurring via hydroxide ion formed by the reaction of amine with adventitious water [Donnelly et al., 1977; Ogawa and Romera, 1977].

The initiator required to polymerize a monomer depends on the reactivity of the monomer toward nucleophilic attack. Monomer reactivity increases with increasing ability to stabilize the carbanion charge. Very strong nucleophiles such as amide ion or alkyl carbanion are needed to polymerize monomers, such as styrene and 1,3-butadiene, with relatively weak electron-withdrawing substituents. Weaker nucleophiles, such as alkoxide and hydroxide ions, can polymerize monomers with strongly electron-withdrawing substituents, such as acrylonitrile, methyl methacrylate, and methyl vinyl ketone, although the efficiency is lower than that of the stronger nucleophiles. A monomer, such as methyl α -cyanoacrylate, with two electron-withdrawing substituents can be polymerized with very mild nucleophiles such as Br^- , CN^- , amines, and phosphines. This monomer, used in many so-called superglues, polymerizes on contact with many surfaces. Polymerization probably involves initiation by water (or OH^- from water) [Donnelly et al., 1977].

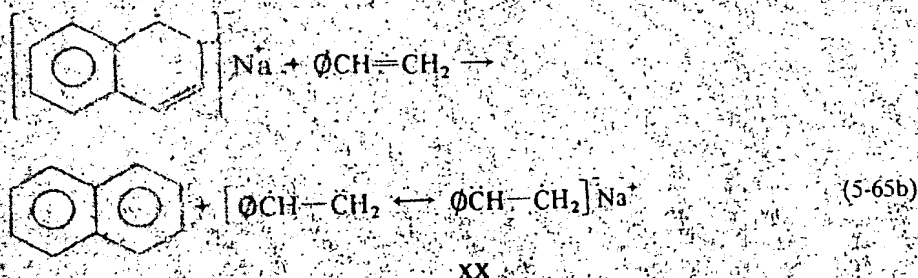
5-3a-2. Electron Transfer

Szwarc and co-workers have studied the interesting and useful polymerizations initiated by aromatic radical anions such as sodium naphthalene [Szwarc, 1968, 1974, 1983]. Initiation proceeds by the prior formation of the active initiator, the naphthalene radical anion ($\text{N}^{\cdot-}$).

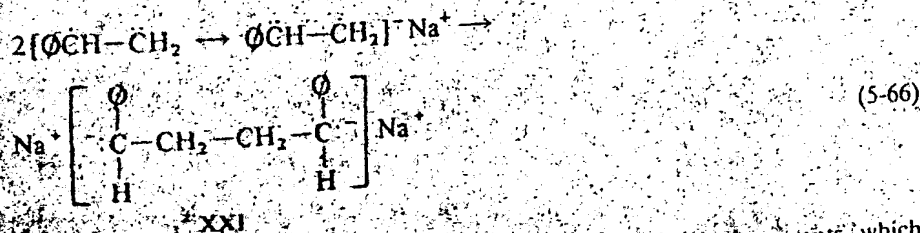


The reaction involves the transfer of an electron from the alkali metal to naphthalene. The radical nature of the anion-radical has been established from electron spin resonance spectroscopy and the carbanion nature by their reaction with carbon dioxide to form the carboxylic acid derivative. The equilibrium in Eq. 5-65a depends on the electron affinity of the hydrocarbon and the donor properties of the solvent. Biphenyl is less useful than naphthalene since its equilibrium is far less toward the anion-radical than for naphthalene. Anthracene is also less useful even though it easily forms the anion-radical. The anthracene anion-radical is too stable to initiate polymerization. Polar solvents are needed to stabilize the anion-radical, primarily via solvation of the cation. Sodium naphthalene is formed quantitatively in tetrahydrofuran (THF), but dilution with hydrocarbons results in precipitation of sodium and regeneration of naphthalene. For the less electropositive alkaline-earth metals, an even more polar solvent than THF [e.g., hexamethylphosphoramide (HMPA)] is needed.

The naphthalene anion-radical (which is colored greenish-blue) transfers an electron to a monomer such as styrene to form the styryl radical-anion (XX).

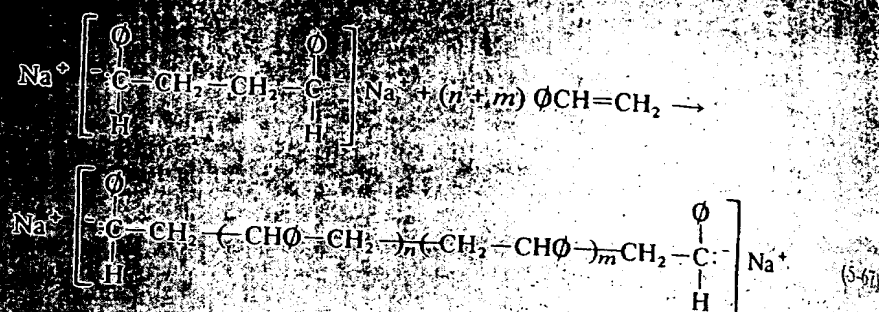


The styryl radical-anion is shown as a resonance hybrid of the forms wherein the anion and radical centers are alternately on the α - and β -carbon atoms. The styryl radical-anion dimerizes to form the dicarbanion (XXI).



That this reaction occurs is shown by electron spin resonance measurements, which indicate the complete disappearance of radicals in the system immediately after the addition of monomer. The dimerization occurs to form the styryl dicarbanion instead of $\text{XII}(\text{C}_6\text{H}_5\text{CH}^-\text{CH}_2)_2$ since the former is much more stable. The styryl dianions so formed are colored red, the same as styryl monocarbanions formed via initiators.

such as *n*-butyllithium). Anionic propagation occurs at both carbanion ends of styryl dianion



Although the suggestion that the styryl anion-radical adds a few monomer molecules prior to dimerization has not been discounted, the reaction kinetics (Sec. 5-3d) clearly show that better than 99% of the propagation occurs through the dianion. Dimerization of radical centers is highly favored by their high concentrations, typically 10^{-3} – $10^{-4} M$ (much higher than in a radical polymerization) and the large rate constants (10^7 – 10^8 liters/mole-sec) for radical coupling [Wang et al., 1978, 1979].

Electron-transfer initiation from other radical-anions, such as those formed by reaction of sodium with nonenolizable ketones, azomethines, nitriles, azo and azoxy compounds, has also been studied. In addition to radical-anions, initiation by electron transfer has been observed when one uses certain alkali metals in liquid ammonia. Polymerizations initiated by alkali metals in liquid ammonia proceed by two different mechanisms. In some systems, such as the polymerizations of styrene and methacrylonitrile, by potassium, the initiation is due to amide ion formed in the system [Overberger et al., 1960]. Such polymerizations are analogous to those initiated by alkali amides. Polymerization in other systems cannot be due to amide ion. Thus polymerization of methacrylonitrile by lithium in liquid ammonia proceeds at a much faster rate than that initiated by lithium amide in liquid ammonia [Overberger et al., 1959]. The mechanism of polymerization is considered to involve the formation of a solvated electron.



Such ammonia solutions are noted by their characteristic deep blue color. The solvated electron is then transferred to the monomer to form a radical-anion,

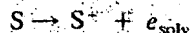


The radical-anion proceeds to propagate in the same manner as discussed above for initiation by sodium naphthalene. (Polymerizations in liquid ammonia are very different from those in organic solvents in that free ions probably constitute the major portion of propagating species.)

Electron-transfer initiation also occurs in heterogeneous polymerizations involving dispersions of an alkali metal in monomer. Initiation involves electron transfer from the metal to monomer followed by dimerization of the monomer radical-anion to form the propagating dianion [Fontanille, 1989; Gaylord and Dixit, 1974; Morton and Fetters, 1977]. The rate of initiation is dependent on the surface area of the metal

since the reaction is heterogeneous. Increased surface area of metal is achieved by condensing metal vapors directly into a reaction mixture or as a thin coating (mirror) of the metal on the inside walls of the reaction vessel or simply using small particle size of the metal.

Initiation by ionizing radiation occurs by electron transfer. Some component of the reaction system; either the solvent or monomer, undergoes radiolysis



(5-70)

to yield a cation-radical and solvated electron [Stannett et al., 1989]. If a monomer of the electron to monomer followed by dimerization to the dicarbanion and propagation (Sec. 5-2a-3-d).

Electroinitiated polymerization proceeds by direct electron-addition to monomer to generate the monomer anion-radical, although initiation in some systems may involve the formation of an anionic species by electrolytic reaction of some component of the reaction system (often, the electrolyte) [Olaj, 1987].

5-3b Termination

5-3b-1 Polymerizations without Termination

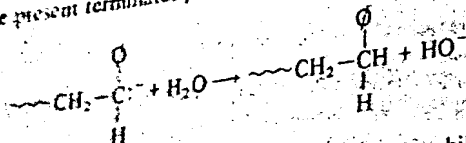
Termination of a propagating carbanion by combination with the counterion occurs in only a few instances, such as in electroinitiated polymerization when the contents of the anode and cathode chambers are mixed and in initiation by ionizing radiation. Termination by combination of the anion with a metal counterion does not take place. Many anionic polymerizations, especially of nonpolar monomers such as styrene and 1,3-butadiene, take place under conditions in which there are no effective termination reactions. Propagation occurs with complete consumption of monomer to form living polymers. The propagating anionic centers remain intact because transfer of proton or other positive species from the solvent does not occur. Living polymers are produced as long as one employs solvents, such as benzene, tetrahydrofuran, and 1,2-dimethoxyethane, which are relatively inactive in chain transfer with carbanions. The polymerization of styrene by amide ion in liquid ammonia, one of the first anionic systems to be studied in detail, is one of the few anionic polymerizations where chain transfer to solvent is extensive [Higginson and Wooding, 1952].

The nonterminating character of living anionic polymerizations is apparent in several different ways. Many of the propagating carbanions are colored. If a reaction system is highly purified so that impurities are absent, the color of the carbanions is observed to persist throughout the polymerization and does not disappear or change at 100% conversion. Further, after 100% conversion is reached, additional polymerization can be effected by adding more monomer, either the same monomer or a different monomer. The added monomer is also polymerized quantitatively and the molecular weight of the living polymer is increased.

5-3b-2 Termination by Impurities and Deliberately Added Transfer Agents

Most anionic (as well as cationic) polymerizations are carried out in an inert atmosphere with rigorously cleaned reagents and glassware since trace impurities lead to termination. Moisture adsorbed on the surface of glassware is usually removed by

flaming under vacuum or washing with a living polymer solution. Oxygen and carbon dioxide from the atmosphere add to propagating carbanions to form peroxy and carboxyl anions. These are normally not reactive enough to continue propagation. (The peroxy and carboxyl anions usually are finally obtained as HO and HOO groups when a proton donor is subsequently added to the polymerization system.) Any radicals present terminates propagating carbanions by proton transfer.

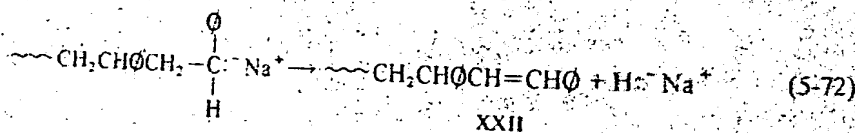


The hydroxide ion is usually not sufficiently nucleophilic to reinitiate polymerization and the kinetic chain is broken. Water has an especially negative effect on polymerization, since it is an active chain-transfer agent. For example, $C_{n,s}$ is approximately 10 in the polymerization of styrene at 25°C with sodium naphthalene [Szwarc, 1966] and the presence of even small concentrations of water can greatly limit the polymer molecular weight and polymerization rate. The adventitious presence of other proton donors may not be as much of a problem. Ethanol has a transfer constant of about 10. Its presence in small amounts would not prevent the formation of high polymer because transfer would be slow, although the polymer would not be living.

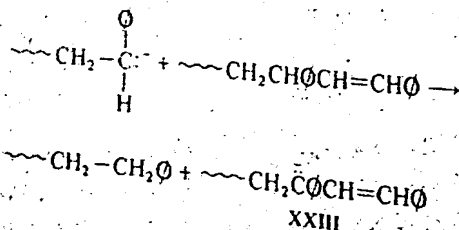
Living polymers are terminated by the deliberate addition of a chain-transfer agent such as water or alcohol to the reaction system after all of the monomer has reacted.

5-3b-3 Spontaneous Termination

Living polymers do not live forever. In the absence of terminating agents, the concentration of carbanion centers decays with time [Fontanille, 1989; Glasse, 1983]. Polystyryl carbanions are the most stable of all living anionic systems, as they are stable for weeks in hydrocarbon solvents. (This is much more stable than any of the living cationic systems studied to date; see Sec. 5-2g). The mechanism for the decay of polystyryl carbanions on aging, referred to as *spontaneous termination*, is not completely established. The generally accepted mechanism, based on spectroscopy (IR, UV-visible) of the reaction system and final polymer after treatment with water, consists of *hydride elimination*



followed by abstraction of an allylic hydrogen from XXII by a carbanion center to yield the unreactive 1,3-diphenylallyl anion (XXIII) [Spach et al., 1962]. The sodium



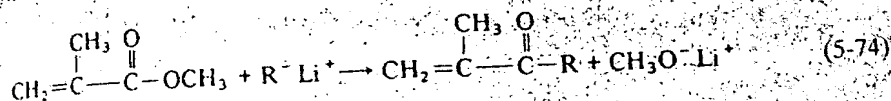
oxide eliminated in Reaction 5-72 may also participate in hydrogen abstraction from

XVII. The stability of polystyryl carbanions is considerably lower in polar solvents with decay occurring over the course of a few days at room temperature, but the stability is considerably better at lower temperatures. Termination in polar solvents (ethers such as THF and 1,2-dimethoxyethane) probably involves α -hydrogen abstraction and/or nucleophilic attack on the C-O bond. The living polymers of 1,3-butadiene and isoprene decay much faster than polystyryl carbanions.

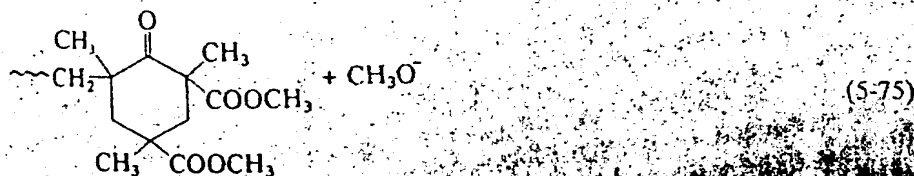
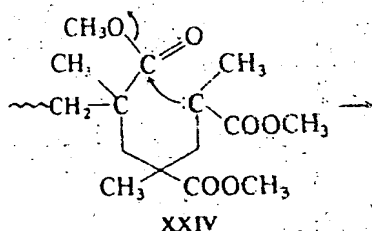
5-3b-4. Terminating Reactions of Polar Monomers

The anionic polymerizations of polar monomers, such as methyl methacrylate, methyl vinyl ketone, and acrylonitrile, are less understood than those for the nonpolar monomers. The polar monomers contain substituents that are reactive toward nucleophiles. This leads to termination and side reactions competitive with both initiation and propagation, resulting in complex polymer structures [Bywater, 1975, 1985; Hogen-Esch and Smid, 1987; Müller, 1989; Müller et al., 1986; Warzelhan et al., 1978]. Living polymerizations are much less frequently encountered.

Several different nucleophilic substitution reactions have been observed in the polymerization of methyl methacrylate. Attack of initiator on monomer



converts the active alkyl lithium to the less active alkoxide initiator. Further, methyl methacrylate (MMA) is converted to *i*-propenyl alkyl ketone to the extent that this reaction occurs. The resulting polymerization is a copolymerization between the two monomers, not a homopolymerization of MMA. More importantly, this results in a slower reaction (and lower polymer molecular weight) since the carbanion derived from the ketone is not as reactive as the carbanion from MMA. Nucleophilic substitution by intramolecular backbiting attack of a propagating carbanion

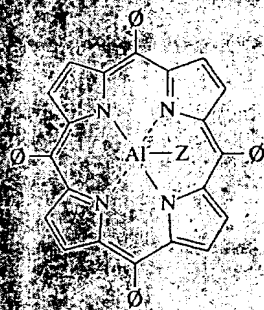


lowers the polymer molecular weight and decreases the polymerization rate since methoxide is a weak initiator. Other reactions have been proposed—nucleophilic

attack by a propagating carbanion on monomer to displace methoxide and yield polymer with an *t*-propenyl keto end group and the intermolecular analogue of Reaction 5-73 to yield branched polymer—but there is little supportive data.

The side reactions, which not only lower the polymerization rate and polymer molecular weight but also broaden the molecular-weight distribution, predominate over "normal" polymerization in hydrocarbon solvents. Reaction 5-74 is the major reaction when butyllithium is used as the initiator with less than 1% of the initiator resulting in high-molecular-weight polymer. This reaction can be significantly minimized but not completely eliminated by using a less nucleophilic initiator, such as diphenylmethylolithium, cumylolithium, or polystyryl carbanions to which a few units of α -methylstyrene have been added (Wiles and Bywater, 1965). However, Reaction 5-75 as well as the other side reactions can be sufficiently minimized by using the less nucleophilic initiator in a polar solvent such as THF at low temperatures (≤ -20 to -70°C) to obtain living polymerizations of acrylate and methacrylate monomers. The addition of a common ion (e.g., by using a mixture of alkylolithium and LiCl) to decrease the nucleophilicity of the propagating centers by forming tighter ion pairs also increases the tendency toward living polymerizations (Fayt et al., 1987; Treysie et al., 1990; Varshney et al., 1990).

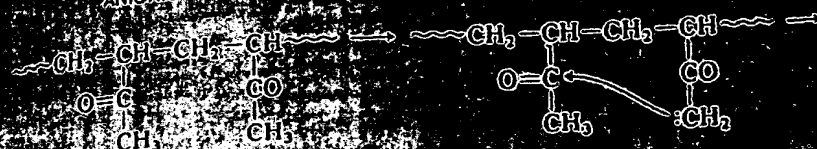
Porphinatoaluminum compounds of structure XXIV ($Z = \text{CH}_3, \text{SO}$) are reported to initiate the living polymerizations of acrylate and methacrylate monomers at



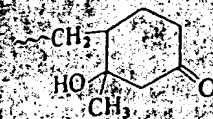
XXIV

temperatures as high as 35°C in methylene chloride [Inoue et al., 1990; Kuroki et al., 1990]. The propagating centers are sufficiently unreactive in side reactions but sufficiently reactive in propagation to allow polymerization in nonpolar solvent without the need for low temperatures. Propagation probably proceeds through covalent species with monomer insertion at $\text{Al}-\text{C}$ bonds. Further discussion of these initiators is found in Sec. 7-2a-1.

Polymerizations of vinyl ketones such as methyl vinyl ketone are also complicated by nucleophilic attack of the initiator and propagating carbanion at the carbonyl group although few details have been established [Dotcheva and Tsvetanov, 1985; Hrdlovic et al., 1979; Nasrallah and Baylouzian, 1977]. Nucleophilic attack in these polymers yields substitution, while that at the ester carbonyl of acrylates and methacrylates yields saponification. The major side reaction is an intramolecular Aldol-type condensation. Abstraction of an α -hydrogen from a methyl group of the polymer by either initiator or propagating carbanion yields an α -carbanion that attacks the carbonyl group of the adjacent repeat unit.



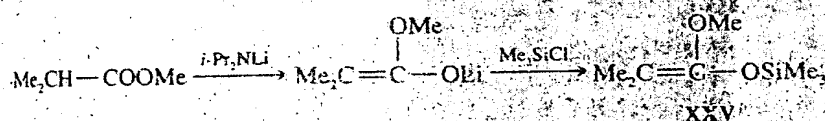
(5-76)



Acrylonitrile polymerization is similarly complicated by addition reactions of the initiator and/or propagating nucleophiles with the nitrile group [Berger and Adler, 1986; Tsvetanov, 1979; Vankerckhoven and Van Beylen, 1978].

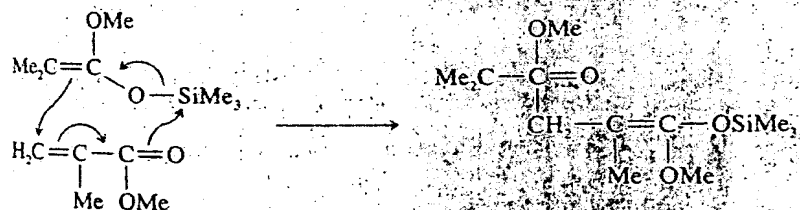
5.3c Group Transfer Polymerization

Although living anionic polymerizations of methacrylates and acrylates can be achieved at low temperatures, the low temperatures limit the practical utility of such processes. Group transfer polymerization yields living polymerizations without resorting to low temperatures [Muller, 1990; Reetz, 1988; Schubert and Bändermann, 1989; Schubert et al., 1989; Shen et al., 1989; Sogah et al., 1987, 1990; Webster, 1987]. The initiator is a silyl ketene acetal (XXV) that is typically synthesized from an ester enolate



(5-77)

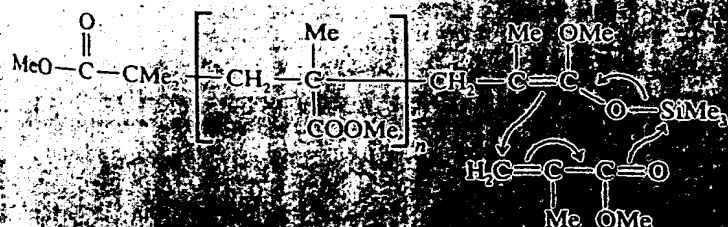
Initiation involves a concerted addition of methyl trimethylsilyl dimethyl ketene acetal to monomer to form species XXVI. The overall effect is to transfer the silyl ketene



(5-78)

XXVI

acetal center from initiator to monomer. Propagation proceeds in a similar manner



(5-79)

with the ketene acetal double bond acting as the propagating center. The proposed mechanism for both initiation and propagation involves nucleophilic attack of the electrons of the ketene acetal on monomer.

Group transfer polymerization (GTP) requires either a nucleophilic or Lewis acid catalyst. Bifluoride (HF_2^-) and fluoride ions, supplied by soluble reagents such as tris(dimethylamino)sulfonium bifluoride, $[(\text{CH}_3)_2\text{N}]_3\text{SHF}_2$, and $(n\text{-C}_4\text{H}_9)_4\text{NF}$, are the most effective nucleophilic catalysts, although other nucleophiles (CN^- , acetate, *p*-nitrophenolate) are also useful. Zinc chloride, bromide, and iodide, and dialkyl aluminum chloride have been used as Lewis acid (electrophilic) catalysts. Nucleophilic catalysts function by assisting in the displacement of the trimethylsilyl group and are effective at low concentrations (<0.1 mole % relative to initiator). Lewis acid catalysts probably function by coordination with the carbonyl oxygen of monomer to increase the electrophilicity of the double bond; making the latter more susceptible to nucleophilic attack. Much higher concentrations of Lewis acid catalysts are needed, 10–20 mole % based on initiator for the aluminum catalysts but 10–20 mole % based on monomer for the zinc catalysts.

Group transfer polymerization requires the absence of materials such as water with active hydrogens, but oxygen does not interfere with the reaction. The range of solvents suitable for GTP is wider than for other anionic polymerizations. *N,N*-Dimethylformamide has been used for polymerizations with nucleophilic catalysts, and chlorinated hydrocarbons as well as acetonitrile for polymerizations with Lewis acid catalysts, although ethers such as tetrahydrofuran and aromatics such as toluene are probably the most commonly used solvents. The concerted nature of the reaction with the absence of full-fledged anionic propagating centers appears responsible for the ability to carry out polymerization in the more active solvents. Solvents such as chlorinated hydrocarbons and DMF cannot be used in anionic polymerizations initiated by sodium naphthalene, alkyl lithium, and similar initiators because of nucleophilic reactions between solvent and initiator. The concerted reaction is also assumed to be responsible for the lowered sensitivity of GTP toward the various side reactions present in the usual anionic polymerization. The same side reactions occur as with anionic polymerization [Brittain and Dicker, 1989], but their rates relative to propagation are lower. This allows living polymerizations to be achieved at higher reaction temperatures. Living polymerizations of methacrylates have been successful at temperatures of 0–50°C. Lower reaction temperatures ($<0^\circ\text{C}$) are required to obtain living systems with acrylate monomers since they are typically more reactive than methacrylates toward both polymerization and side reactions.

Control of polymer molecular weight can be achieved readily up to molecular weights of 10,000 to 20,000. Higher molecular weights require highly purified reagents as in other anionic polymerizations and the use of nucleophilic catalysts. The large amounts of Lewis acid catalysts required increases the extent of termination. Further, Lewis acid catalysts have a large disadvantage in terms of the purification required to obtain a product free of inorganic materials.

The concerted mechanism has been questioned for nucleophile-catalyzed group transfer polymerization [Quirk and Bidinger, 1989]. The alternate mechanism proposed for GTP involves a generation of the usual anionic propagating species in low concentrations by nucleophilic displacement of the trimethyl silyl group of initiator by the nucleophilic catalyst. The key to control of termination by side reactions in this mechanism involves a reversible complexation of the low concentration of propagating centers by the high concentration of silyl ketene acetal polymer chain ends. This

propagation of GTP, referred to as *aldol GTP*, involves polymerization of a silyl vinyl ether by an aldehyde [Sogah and Webster, 1986; Webster, 1987]. Both initiation and propagation involve nucleophilic addition of the vinyl ether to the aldehyde carbonyl group with transfer of the trialkyl silyl group from vinyl ether to the carbonyl oxygen (Eq. 5-80a). The reaction has similar characteristics as GTP. The



5-3d Kinetics of Polymerization with Termination

(5-81a)



(5-82)

or

$$R_i = \frac{k_i K [M] [KNH_2]}{[K^+]}$$

(S-83)

Propagation proceeds according to

(S-84)



with a rate given by

(S-85)

$$R_p = k_p [M^-] [M]$$

where $[M^-]$ represents the total concentration of the propagating anionic centers.
Chain transfer to solvent



is extensive but does not terminate the kinetic chain since amide ion is regenerated.
Termination occurs by transfer to adventitious water.



or other impurity present. The rates of Reactions S-86 and S-87 are given by

$$R_{p, NH_3} = k_{ct} [M^-] [NH_3]$$

(S-88)

$$R_{p, H_2O} = k_{tw} [M^-] [H_2O]$$

(S-89)

The polymerization rate, derived in the usual manner by combining Eqs. S-82, S-83, S-85, and S-89 with the assumption of a steady state for $[M^-]$, is obtained as

$$R_p = \frac{k_i k_p [M] [KNH_2]}{k_t [K^+] [H_2O]}$$

(S-90)

The number-average degree of polymerization is given by

$$\frac{1}{\bar{X}_n} = \frac{C_{NH_3} [NH_3]}{C_M [M]} + \frac{C_{H_2O} [H_2O]}{C_M [M]}$$

(S-91)

Amide ion-initiated polymerizations in liquid ammonia are about the only anionic polymerizations studied that proceed without termination.

5-3e. Kinetics of Living Polymerization

5-3e-1. Polymerization Rate

The rate of polymerization in nonterminating systems can be expressed as the rate of propagation:

$$R_p = k_p [M^-] [M]$$

(S-92)

where $[M^-]$ is the total concentration of all types of living anionic propagating centers (free ions and ion pairs). $[M^-]$ can be determined by reacting the living polymer with a terminating agent such as methyl iodide, carbon dioxide, or other electrophilic substance followed by analysis of the amount of terminating agent incorporated into the polymer. The use of isotopically labeled terminating agents can increase the analytical sensitivity. Ultraviolet-visible spectroscopy is also useful for determining the total concentration of propagating species. Since free ions constitute a very small percentage of $[M^-]$ for most systems, equating the concentration of ion pairs with $[M^-]$ does not introduce a significant error. The living ends are monoanions in polymerizations initiated by butyllithium and similar initiators and dianions in polymerizations initiated by electron transfer. The two types of anions are referred to as *one-ended* (monofunctional) and *two-ended* (bifunctional) living anions.

Equation 5-92 applies for the case where initiation is rapid relative to propagation. This condition is met for polymerizations in polar solvents. However, polymerizations in nonpolar solvent frequently proceed with an initiation rate that is of the same order of magnitude or lower than propagation. More complex kinetic expressions analogous to those developed for radical and nonliving cationic polymerizations apply for such systems [Pepper, 1980; Szwarc et al., 1987].

As with certain cationic systems, many anionic living polymerizations proceed too rapidly to be followed by techniques such as dilatometry. The stopped-flow technique (Sec. 5-2e-1) is useful for studying these fast polymerizations. Ultraviolet-visible spectroscopy of the rapidly mixed reaction system contained in a capillary tube allows one to follow the initiation rate (observing the increase in optical density of propagating species) and/or the polymerization rate (by following loss of monomer). The polymerization rate can also be obtained by a modification of the apparatus in which polymerization is stopped by running the contents of the capillary tube into a solvent containing a terminating agent. The reaction time is given by the ratio of the capillary volume to the flow rate. Short reaction times from 0.005 to 2 sec can be accurately studied in this manner. The conversion and, hence, R_p and apparent propagation rate constant are obtained by analyzing the quenched reaction mixture for either polymer or unreacted monomer.

It is useful to understand the reasons for the faster reaction rates encountered in many anionic polymerizations compared to their radical counterparts. This can be done by comparing the kinetic parameters in appropriate rate equations: Eq. 3-22 for radical polymerization and Eq. 5-92 for anionic polymerization. The k_p values in radical polymerization are similar to the k_p^{app} values in anionic polymerization. Anionic k_p^{app} values may be 10- to 100-fold lower than in radical polymerization for polymerization in hydrocarbon solvents, while they may be 10- to 100-fold higher for polymerizations in ether solvents. The major difference in the rates of anionic and radical polymerizations resides in the lack of termination in anionic polymerization and the large difference in the concentrations of the propagating species. The concentration of propagating radicals is 10^{-9} – 10^{-7} M, while that for propagating anions is often as high as 10^{-4} – 10^{-2} M. Thus anionic polymerization rates are much higher than radical rates based only on the concentrations of propagating species.

5-3e-2 Effects of Reaction Media

The propagation rate constant and the polymerization rate for anionic polymerization are dramatically affected by the nature of both the solvent and the counterion. Thus the data in Table 5-10 show the pronounced effect of solvent in the polymerization of styrene by sodium naphthalene (3×10^{-3} M) at 25°C. The apparent propagation rate

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TABLE 5-10 Effect of Solvent on Anionic Polymerization^a of Styrene

Solvent	Dielectric Constant (ε)	k _p ^{app} liters/mole-sec
Benzene	2.2	2
Dioxane	2.2	5
Tetrahydrofuran	7.6	550
1,2-Dimethoxyethane	3.5	3,800

^aData from Szwarc and Smid (1954)

constant is increased by two and three orders of magnitude in tetrahydrofuran and 1,2-dimethoxyethane, respectively, compared to the rate constants in benzene and dioxane. The polymerization is much faster in the more polar solvents. That the dielectric constant is not a quantitative measure of solvating power is shown by the higher rate in 1,2-dimethoxyethane (DME) compared to tetrahydrofuran (THF). The faster rate in DME may be due to a specific solvation effect arising from the presence of two ether functions in the same molecule.

The increase in k_p^{app} with increased solvating power of the reaction medium is due mainly to the increased fraction of free ions present relative to ion pairs. It would be more informative to obtain the individual propagation rate constants for the free ions and ion pairs as well as the relative amounts of the two types of propagating species.

5-3e-2-a Evaluation of Individual Propagation Rate Constants for Free Ions and Ion Pairs. The rate of polymerization is appropriately expressed as the sum of the rates for the free propagating anion P⁻ and the ion pair P⁻(C⁺):

$$R_p = k_p^-[P^-][M] + k_p^-[P^-(C^+)] [M] \quad (5-93)$$

where k_p⁻ and k_p⁻ are the propagation rate constants for the free ion and ion pair, respectively. [P⁻] and [P⁻(C⁺)] are the concentrations of the free ion and ion pair, and [M] is the monomer concentration. C⁺ in the above notation is the positive counterion. Comparison of Eqs. 5-92 and 5-93 yields the apparent k_p^{app} as

$$k_p^{app} = \frac{k_p^-[P^-] + k_p^-[P^-(C^+)]}{[M^-]} \quad (5-94)$$

The two propagating species are in equilibrium according to



governed by the dissociation constant K given by

$$K = \frac{[P^-][C^+]}{[P^-(C^+)]} \quad (5-96)$$

For the case where [P⁻] = [C⁺], that is, there is no source of either ion other than P⁻(C⁺), the concentration of free ions is

$$[P^-] = (K[P^-(C^+)])^{1/2} \quad (5-97)$$

The extent of dissociation is small under most conditions; the concentration of ion pairs is close to the total concentration of living ends and Eq. 5-97 can be rewritten as

$$[P^-] = (K[M^-])^{1/2} \quad (5-98)$$

The concentration of ion pairs is given by

$$[P^-(C^+)] = [M^-] - (K[M^-])^{1/2} \quad (5-99)$$

Combination of Eqs. 5-94, 5-98, and 5-99 yields k_p^{app} as a function of $[M^-]$

$$k_p^{app} = k_p^- + \frac{(k_p^- - k_p^+)K^{1/2}}{[M^-]^{1/2}} \quad (5-100)$$

Polymerizations can also be carried out in the presence of excess counterion by adding a strongly dissociating salt (e.g., $NaB\phi_4$ to supply excess Na^+). The concentration of free ions, depressed by the common ion effect, is given by

$$[P^-] = \frac{K[M^-]}{[C^+]} \quad (5-101)$$

When the added salt is strongly dissociated and the ion pairs slightly dissociated, the counterion concentration is very close to that of the added salt $[CZ]$

$$[C^+] = [CZ] \quad (5-102)$$

The concentrations of free anions and ion pairs are given by

$$[P^-] = \frac{K[M^-]}{[CZ]} \quad (5-103)$$

$$[P^-(C^+)] = [M^-] - \frac{K[M^-]}{[CZ]} \quad (5-104)$$

which are combined with Eq. 5-94 to yield

$$k_p^{app} = k_p^- + \frac{(k_p^- - k_p^+)K}{[CZ]} \quad (5-105)$$

Equations 5-100 and 5-105 allow one to obtain k_p^- , k_p^+ , and K from k_p^{app} values obtained in the absence and presence of added common ion. A plot of k_p^{app} obtained in the absence of added common ion versus $[M^-]^{-1/2}$ yields a straight line whose slope and intercept are $(k_p^- - k_p^+)K^{1/2}$ and k_p^- , respectively. A plot of k_p^{app} obtained in the presence of added common ion versus $[CZ]^{-1}$ yields a straight line whose slope and intercept are $(k_p^- - k_p^+)K$ and k_p^- , respectively. Figures 5-5 and 5-6 show these plots for polystyryl sodium in 3-methyltetrahydrofuran at 20°C. The combination of the two slopes and two intercepts allows the individual calculation of k_p^- , k_p^+ , and K . (Note: K as well as $[P^-]$ and $[P^-(C^+)]$ can also be independently determined from conductivity measurements.)

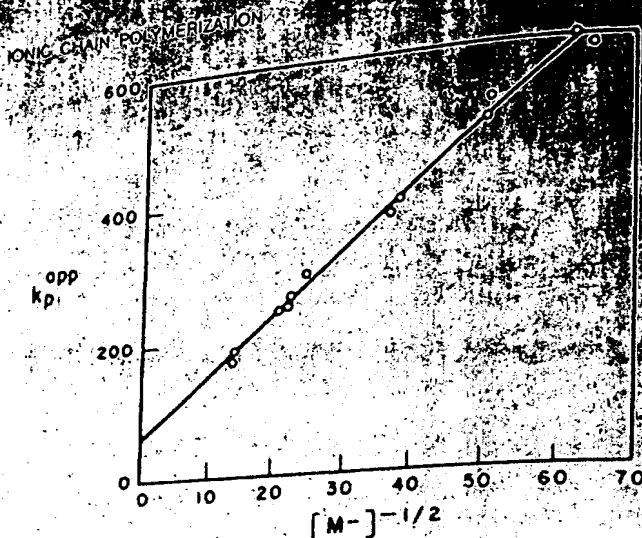


Fig. 5-5. Polymerization of styrene by sodium naphthalene in 3-methyltetrahydrofuran at 20°C. After Schmitt and Schulz [1975] (by permission of Pergamon Press Ltd., Oxford).

5-3e-2-b *Reactivity in Anionic Polymerization.* Table 5-11 shows the values of K and the propagation rate constants for free ions and ion pairs in styrene polymerization in THF at 25°C with various alkali metal counterions [Bhattacharyya et al., 1965a,b]. The corresponding k_p^+ values in dioxane are also presented. The values of K and k_p^+ in dioxane could not be obtained as conductivity measurements indicated no detectable dissociation of ion pairs to free ions in dioxane. A consideration of the data in Table

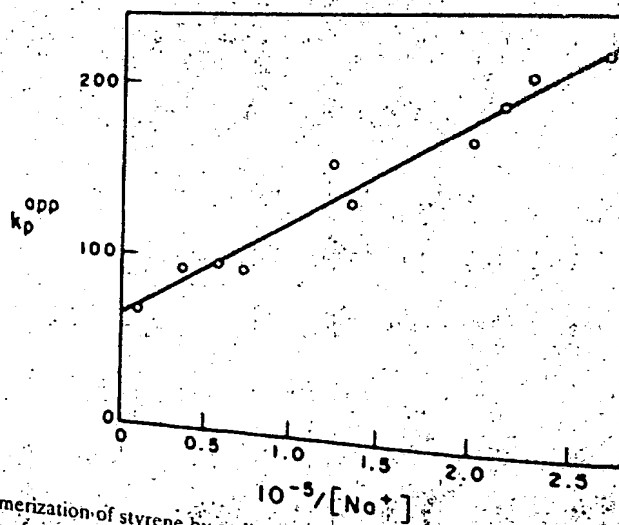


Fig. 5-6. Polymerization of styrene by sodium naphthalene in 3-methyltetrahydrofuran at 20°C in the presence of sodium tetraphenylborate. After Schmitt and Schulz [1975] (by permission of Pergamon Press Ltd., Oxford).

TABLE 5-11. Effect of Counterion on Anionic Polymerization of Styrene^a

Counterion	Polymerization in Tetrahydrofuran			k_p^+ for Dioxane
	k_p^+	$K \times 10^7$	k_p^-	
Li ⁺	160	2.2	6.5×10^4	0.94
Na ⁺	80	1.5		3.4
K ⁺	60-80	0.8		19.8
Rb ⁺	50-80	0.1		21.5
Cs ⁺	22	0.02		24.5

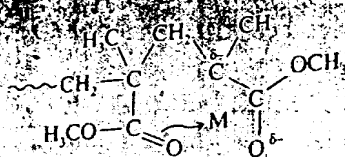
^aData from Bhattacharyya et al. [1965a, 1965b].

5-11; allows an understanding of reactivity in anionic polymerization. The polymerization data shows the much greater reactivity of the free ion compared to any of the ion-pairs. The value of k_p^- is 6.5×10^4 liters/mole-sec which is larger by a factor of 10^3 - 10^5 than the k_p^+ values. Similar differences between k_p^- and k_p^+ have been observed in polymerizations of methyl methacrylate (MMA), 2-vinylpyridine (2VP), and isoprene (IP) [Bywater, 1985; Jeuk and Muller, 1982; Van Beylen et al., 1988]. For reference, k_p^- has values of 3.8×10^3 , 1.0×10^5 , and 2.0×10^3 liters/mole-sec for IP (25°C), 2VP (25°C), and MMA (-98°C), respectively, all measured in THF [Bywater, 1985].

The K values in Table 5-11 indicate that increased solvating power affects the reaction rate primarily through an increase in the concentration of free ions. When lithium is the counterion, one calculates from the equilibrium constant that 1.48% of the propagating centers are free ions in THF (for a system where the total concentration of all propagating centers is $10^{-3} M$) compared to zero in dioxane. Since free ions are so much more reactive than ion pairs, their small concentration has a very large effect on the observed polymerization rate. The majority of the propagation is carried by free ions; only about 10% of the observed reaction rate is due to ion pairs. It is worth mentioning that K values independently measured by conductivity are in excellent agreement with those obtained from the kinetic measurements. The values K from conductivity are 1.9 , 1.5 , 0.7 , and 0.028×10^{-7} , respectively, for lithium, sodium, potassium, and cesium counterions [Geacintov et al., 1962; Shimomura et al., 1967a, 1967b; Szwarc, 1969]. Table 5-11 shows that the dissociation constant for the ion pair decreases in going from lithium to cesium as the counterion. The order of increasing K is the order of increasing solvation of the counterion. The smaller Li⁺ is solvated to the greatest extent and the larger Cs⁺ is the least solvated. The decrease in K has a very significant effect on the overall polymerization, since there is a very significant change in the concentration of the highly reactive free ions. Thus the free-ion concentration for polystyryl cesium ($K = 0.02 \times 10^{-7}$) is less than 10% that of polystyryl lithium ($K = 10^{-7}$).

The reactivities of the various ion pairs also increase in the same order as the K values: Li⁺ > Cs⁺. The fraction of the ion pairs that are of the solvent-separated type increases with increasing solvation of the counterion. Solvent-separated ion pairs are much more reactive than contact ion pairs (Sec. 5-3e-4). The lower values of k_p^+ in dioxane relative to THF are also a consequence of the presence of a smaller fraction of the more reactive solvent-separated ion pairs. The order of reactivity for the different ion pairs in dioxane is the reverse of that in tetrahydrofuran. Solvation is not important in dioxane. The ion pair with the highest reactivity is that with the weakest bond

between the carbanion center and counterion. The bond strength decreases and reactivity increases with increasing size of counterion. However, the effect of increasing counterion size levels off after K^+ as k_p is approximately the same for potassium, rubidium, and cesium. The effect of counterion on ion-pair reactivity is different for methyl methacrylate (MMA) compared to styrene. The value of k_p is 1 for lithium counterion and 30–33 for the larger alkali metal counterions for polymerization in tetrahydrofuran at -98°C [Jeuk and Muller, 1982; Szwarc, 1983]. The difference between lithium counterion and the larger counterions for MMA in THF is similar to that observed for styrene in dioxane. These results have been interpreted as indicating the absence of solvation by THF for MMA polymerization due to the presence of intramolecular solvation. Intramolecular solvation involves electron donation from the carbonyl oxygen of the penultimate unit (i.e., the unit just before the end unit of the propagating chain) as shown in XXVII [Kraft et al., 1973, 1980]. This additional



XXVII

binding of the counterion to the polymer accounts for the low dissociation constant ($K < 10^{-9}$) for polymethyl methacrylate and also poly(2-vinylpyridine) ion pairs [Tend and Sigwalt, 1972; Van Beylen et al., 1988]. Intramolecular solvation in poly(2-vinylpyridine) involves electron donation from the nitrogen of a penultimate pyridine ring. This effect may also be responsible for the decrease in dissociation constant of the poly(2-vinylpyridine) ion pair with decreasing size of counterion in THF. Thus K is 1.1×10^{-9} , 2.5×10^{-9} , and 8.3×10^{-10} for Cs^+ , K^+ , and Na^+ , respectively [Szwarc, 1983]. This is the reverse of the order observed for polystyrene ion pairs in THF. Apparently, smaller counterions "fit better" or "more tightly" into the intramolecular solvation sphere.

5.3e-3 Degree of Polymerization

The number-average degree of polymerization for a living polymerization is given by the ratio of the concentrations of monomer and living ends [Eq. 5-57]. For the usual situation where all of the initiator I is converted into propagating living anionic ends, Eq. 5-57 becomes

$$\bar{X}_n = \frac{2[M]}{[I]} \quad (5-106)$$

or

$$\bar{X}_n = \frac{[M]}{[I]} \quad (5-107)$$

depending on the mode of initiation. Equation 5-106 applies to polymerization initiated by electron transfer, since each final polymer molecule contains two

initiator molecules (e.g., one dianionic propagating species is formed from two sodium naphthalenes). Initiation processes other than electron transfer (e.g., alkyl lithium) involve one polymer molecule per initiator molecule and Eq. 5-107 is applicable.

Narrow molecular-weight distributions are obtained for systems with fast initiation and efficient mixing in the absence of depropagation, termination, and transfer reactions (Eq. 5-59). *PDI* values below 1.1-1.2 are found for many living polymerizations. The living polymer technique offers a unique method of synthesizing standard polymer samples of known and well-defined molecular weights. Commercially available molecular-weight standards are now available for a number of polymers—polystyrene, polyisoprene, poly(α -methylstyrene), poly(2-vinylpyridine), poly(methyl methacrylate), polyisobutylene, and poly(tetrahydrofuran). All except the last two polymers are synthesized by living anionic polymerization. The last two are obtained by living cationic polymerization with ring-opening polymerization (Chap. 7) used for poly(tetrahydrofuran). These polymer standards are useful as calibration standards in molecular weight measurements by size exclusion chromatography, membrane and vapor pressure osmometry, and viscometry.

The occurrence of any termination, transfer or side reactions result in broadening of the molecular-weight distribution. The termination reactions in methacrylate polymerizations (at other than low temperatures in polar solvents) and depropagation in α -methylstyrene polymerizations broaden *PDI* [Chaplin and Yaddelige, 1980; Malhotra et al., 1977; Malhotra, 1978]. Although the bulk of propagation is carried by a small fraction of the propagating species (i.e., the free ions), this does not significantly broaden the molecular-weight distribution since the free ions and ion pairs are in rapid equilibrium. Each polymer chain propagates as both free ion and ion pair over its lifetime and the average fractions of its lifetime spent as free ion and ion pair are not too different than for any other propagating chain.

5-3e-4 Energetics: Solvent-Separated and Contact Ion Pairs

The data available on the temperature dependence of the rates of living polymerization show the experimental activation energy E_R is generally relatively low and positive. One should note that E_R for living polymerization is the activation energy for propagation. The polymerization rates are relatively insensitive to temperature but increase with increasing temperature. Furthermore, the activation energy varies considerably depending on the solvent employed in the polymerization as was the case for cationic polymerization. Thus the activation energy for propagation in the system styrene-sodium naphthalene is 37.6 kJ/mole in dioxane and only 4.2 kJ/mole in tetrahydrofuran [Allen et al., 1960; Geacintov et al., 1962; Stretch and Allen, 1961]. The molecular weight of the polymer produced in a nonterminating polymerization is unaffected by temperature if transfer agents are absent. The situation can be different if transfer agents are initially present.

Most of the activation energy data reported in the literature are *apparent activation energies* corresponding to the values for the apparent propagation rate constant. The effect of temperature on propagation is complex—temperature simultaneously affects the relative concentrations of free ions and ion pairs and the individual rate constants for the free ions and ion pairs. Temperature affects the rate constants k_p^- and k_p^+ in the manner all rate constants are affected, increasing temperature increases the values of k_p^- and k_p^+ . However, the effect of temperature on the concentration of free ions relative to ion pairs is in the opposite direction. The change with temperature of the

Equilibrium constant for dissociation of ion pairs into free ions is given by the relationship

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

(S-103)

where ΔH is negative and K increases with decreasing temperature [Schmitt and Schulz, 1975; Shimomura et al., 1976b]. For example, ΔH is about -37 kJ/mole for polystyryl sodium in tetrahydrofuran which corresponds to an increase in K by a factor of about 300 as the temperature changes from 25 to -70°C . The free-ion concentration is higher by a factor of about 20 at -70°C compared to 25°C for a living end concentration of 10^{-3} M. The change in K with temperature is less for polystyryl cesium as ΔH is about -8 kJ/mole. The opposing effects of temperature on K and on the propagation rate constants results in apparent activation energies which are often low. Apparent activation energies for propagation in poorer solvating media will be higher than those in better solvating media. Little ionization to free ion takes place in the former and temperature has little effect on K . Significant ionization occurs in better solvents, K changes considerably with temperature, and the effect of T on K may come close to offsetting its effects on k_p^+ and k_p^- . This clearly is the reason why the apparent activation energy for polystyryl sodium is 37.6 kJ/mole in dioxane but only 4.2 kJ/mole in tetrahydrofuran. Similarly, the effect of T on K in more polar solvents is greater for the smaller, better-solvated ions (Na^+) compared to the larger, more poorly solvated ions (Cs^+).

Evaluation of k_p^+ and k_p^- and the corresponding activation parameters has been carried out for polystyryl sodium and cesium in several different ether solvents (THF, tetrahydropyran, 1,2-dimethoxyethane) [Muller, 1989; Schmitt and Schulz, 1975; Szwarc, 1968, 1974, 1983]. k_p^+ is independent of counterion, indicating that the observed value is for the free ion. Further, k_p^+ is independent of the solvent, although one expects a decrease in the rate constant with increasing solvating power for reaction between an ionic species and a neutral molecule (Sec. 5.2f-2). Apparently, the range of solvents studied (various ethers) did not contain a large enough difference in solvating power to observe the expected effect even though there was a significant variation in the dielectric constants of the ethers. The various ethers are assumed to be similar in their specific solvation of the free anionic propagating centers. (One should keep in mind that the range of solvents appropriate to anionic polymerization is quite limited—mostly hydrocarbons and ethers.) The activation energy E_p^+ and the frequency factor A_p^+ for the free ion are 16.7 kJ/mole and 10^8 liters/mole-sec, respectively. It is useful to note that the propagation rate constant for the free polystyryl anion ($k_p^- \approx 10^5$) is larger than that for the free radical (165 liter/mole-sec) by three orders of magnitude. Propagation by the anion is favored by both a lower activation energy and a higher frequency factor ($E_p^- = 26$ and $A_p^- = 4.5 \times 10^8$ for anionic propagation). The lower activation energy for anionic propagation is reasonable, since the interaction between anion and monomer should generate attractive forces (due to polarization) that reduce the potential energy barrier to addition. The more favorable frequency factor results from a decrease in order of the surrounding reaction medium when the negative charge of the propagating anion is dispersed in the transition state. From Table 5.3, we can note that the propagation rate constant for the free polystyryl carbocation is larger than for the carbocation by a factor of $10-100$ as expected. Carbocation addition involves the use of vacant orbitals of the carbocation, while anionic

propagation requires the use of antibonding orbitals, since all bonding orbitals on both monomer and carbanion are filled.

The calculation of k_p^* and the corresponding activation parameters E_p^* and A_p^* proceeds in a reasonably straightforward manner for polymerizations in solvents of low polarity (no higher than dioxane). However, anomalous behavior is observed for polymerizations in solvents which are better solvating media than dioxane. k_p^* is observed to increase with decreasing temperature in some systems, leading to negative activation energies. The activation energy for propagation by polystyryl sodium ion pairs in tetrahydrofuran is -6.2 kJ/mole over the temperature range -80 to 25°C [Shimomura et al., 1967a, 1967b]. E_p^* for poly(α -methylstyryl) sodium in THF is -8.8 kJ/mole over the range -25 to 5°C [Hui and Ong, 1976]. More significantly, experiments carried out over a sufficiently wide temperature range showed that E_p^* changed with temperature. Figure 5-7 shows the Arrhenius plot of k_p^* versus $1/T$ for polystyryl sodium in tetrahydrofuran and 3-methyltetrahydrofuran [Schmitt and Schulz, 1975]. The plots are S-shaped with two inflection points. These anomalous results indicate that two different types of ion pairs are present and undergoing propagation, the contact ion pairs and solvent-separated ion pairs (corresponding to structures II and III in Sec. 5-1).

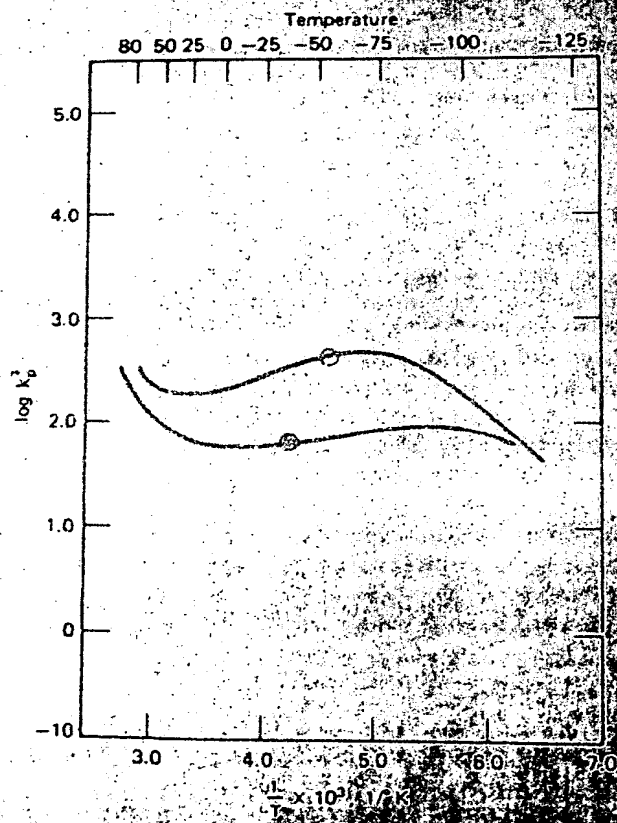


Fig. 5-7 Propagation rates constant for polystyryl sodium ion pairs in tetrahydrofuran (O) and 3-methyltetrahydrofuran (●). After Schmitt and Schulz [1975] (by permission of Pergamon Press Ltd., Oxford).

The observed ion pair propagation constant k_p^{\pm} is an apparent rate constant, a composite of the rate constants for the contact ion pair (k_c) and solvent-separated ion pair (k_s) according to

$$k_p^{\pm} = xk_s + (1-x)k_c \quad (5-109)$$

or

$$k_p^{\pm} = \frac{(k_c + k_s K_{cs})}{(1 + K_{cs})} \quad (5-110)$$

where x and $(1-x)$ are the fractions of solvent-separated and contact ion pairs respectively, and K_{cs} is the equilibrium constant for interconversion between the two types of ion pairs



The variation of k_p^{\pm} with temperature depends on the interplay of the separate variations of k_c , k_s , and K_{cs} on temperature according to

$$\ln k_c = \ln A_c - \frac{E_c}{RT} \quad (5-112)$$

$$\ln k_s = \ln A_s - \frac{E_s}{RT} \quad (5-113)$$

$$\ln K_{cs} = -\frac{\Delta H_{cs}}{RT} + \frac{\Delta S_{cs}}{R} \quad (5-114)$$

A consideration of Eqs. 5-109, 5-110, 5-112, 5-113, and 5-114 indicates the reasons for the behavior observed in Fig. 5-7. There are no solvent-separated ion pairs at the highest temperature (ca. 70°C in THF). Decreasing temperature decreases k_p^{\pm} because k_c is decreasing. As the temperature continues decreasing, a temperature is reached at which solvent-separated ion pairs are formed. Since $k_s > k_c$, k_p^{\pm} goes through a minimum (at ca. 30°C), and then increases (provided $E_s < -\Delta H_{cs}$). However, a further decrease in temperature causes the rate to go through another inflection. There is so much conversion of contact ion pairs to solvent-separated ion pairs that any additional increase in the fraction of the latter is insufficient to counter the conventional effect of E_s ; k_s decreases with decreasing T , k_p^{\pm} reaches a maximum (at ca. -75°C) and then decreases. The overall effect of T on k_p^{\pm} depends on the relative values of E_c , E_s , ΔH_{cs} , and ΔS_{cs} . In a poor solvent such as dioxane, there is a negligible fraction of solvent-separated ion pairs at all temperatures; k_c and k_p^{\pm} decrease with decreasing temperature over the complete temperature range. In a moderately good solvent (THF and 3-methyltetrahydrofuran), the behavior in Fig. 5-7 is observed. For a sufficiently good solvent where the fraction of solvent-separated ion pairs is close to one, k_c and k_p^{\pm} would decrease continuously with decreasing temperature. Data indicate that hexamethylphosphoramide is such a solvent for polystyryl sodium [Schmitt and Schulz, 1975].

Experimental data of k_p^{\pm} versus $1/T$ can be fitted to the preceding equations to

yield values of the various activation and thermodynamic parameters pertinent to ion pair propagation (Table 5-12). Corresponding values of the parameters for free-ion propagation are included in Table 5-12 for comparison. The solvent-separated ion pair is approximately half as reactive as the free ion, while the contact ion pair is more than three orders of magnitude less reactive. The fact that k_p^+ is only slightly more than twice k_p^- clearly indicates that the solvent-separated ion pair is in an environment similar to that of the free ion. The frequency factors for the three types of propagating centers are very similar; reactivity differences are due to the differences in activation energies. The free ion and solvent-separated ion pair have comparable activation energies. The much higher value of E_c indicates the need to separate the anion and counterion in the transition state so that monomer can be inserted. The K_a values show that a large fraction of the ion pairs in THF are solvent-separated ion pairs. Since $k_p^- \gg k_c$, any significant concentration of solvent-separated ion pairs will contribute heavily to the overall propagation rate. The wide variation in the relative amounts of solvent-separated and contact ion pairs with solvent is evident from the values of K_a (0.13, 0.002, 0.0001, and $< 10^{-5}$ for 1,2-dimethoxyethane, tetrahydrofuran, tetrahydropyran, and dioxane, respectively, at 25°C) [Szwarc, 1983].

The reactivity of the solvent-separated ion pair is hardly affected by the counterion. This can be observed from the k_p^+ values in THF (Table 5-11). Most of the observed propagation in THF is due to solvent-separated ion pairs and k_p^+ is a good indication of k_p^- . The variation in k_p^+ from Li^+ to Cs^+ is relatively small and is probably due more to differences in the fractions of solvent-separated ion pairs than to differences in k_p^- . The reactivity of contact ion pairs is more sensitive to the counterion. The variation of k_p^+ in dioxane is by a factor of 25 between the different counterions. Since the fraction of solvent-separated ion pairs is extremely small in dioxane, k_p^+ is indicative of k_c . The larger, more loosely held cesium counterion results in a higher reactivity for the contact ion pair. The variation of k_c and k_i with solvating power of the reaction medium is not established. Some data indicate that k_c is insensitive to solvent while k_i increases with increasing solvating power, but these results are limited to ether solvents.

TABLE 5-12 Propagation of Polystyryl Sodium in Tetrahydrofuran^a

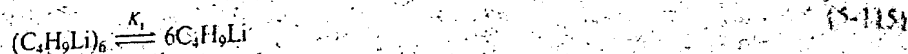
k_p^- (20°C)	1.5×10^5 liters/mole-sec
K (20°C)	4.0×10^{-4} mole/liter (20°C)
	79.1×10^{-4} mole/liter (-48°C)
E_p^-	16.6 kJ/mole
A_p^-	1.0×10^6 liters/mole-sec
E_c	36.0 kJ/mole
A_c	6.3×10^5 liters/mole-sec
k_i (20°C)	24 liters/mole-sec
E_i	19.7 kJ/mole
A_i	2.08×10^6 liters/mole-sec
k_p^+ (20°C)	5.5×10^4 liters/mole-sec
ΔH_a	-19.7 kJ/mole
ΔS_a	-132 J/K mole
K_a	2.57×10^{-1} (20°C)
	2.57×10^{-2} (-50°C)

^aData for Schmitt and Schulz [1975].

5-3e-5 Association Phenomena in Alkylolithium

A complication for polymerizations initiated by organolithium compounds in nonpolar solvents, such as cyclohexane, *n*-hexane, and benzene, is association (aggregation) of the various organolithium species present in the reaction system. Association occurs with organolithium compounds because of the small size of lithium and its possession of more low energy orbitals than electrons. Each lithium associates and participates in bonding with two or more organic moieties. The phenomenon is important since the associated species are far less reactive than unassociated species in initiation and propagation. The effects of association have been extensively studied for styrene, isoprene, and 1,3-butadiene polymerizations initiated by *n*-, *i*-, and *t*-butyllithium, but there are considerable discrepancies between the results and mechanistic interpretations of different workers [Bywater, 1975, 1985; Morton, 1983; Van Beylen et al., 1988; Young et al., 1984].

The initiation and propagation reactions are typically found to show fractional orders of dependence of rate on alkylolithium. The situation is quite complex. The fractional orders for initiation and propagation are usually not the same and often vary depending on the monomer, solvent, and initiator and their absolute as well as relative concentrations. For styrene polymerization by *n*-butyllithium in aromatic solvents, the initiation and propagation rates are proportional to only the 1/2 and 1/3 powers of *n*-butyllithium concentration, respectively. These results have been interpreted in terms of the following association equilibria



with initiator and propagating ion pairs in equilibria with the unassociated hexamer and dimer, respectively. (Equation 5-115 is an oversimplified representation of hexamer to monomeric *n*-butyllithium probably taking place in two steps.) One derives the concentrations of unassociated initiator and propagating species as follows:

$$[C_4H_9Li] = K_1^{1/6} [(C_4H_9Li)_6]^{1/6} \quad (5-117)$$

$$[C_4H_9-M_nLi^*] = K_2^{1/2} [(C_4H_9-M_nLi^*)_2]^{1/2} \quad (5-118)$$

which explain the dependence of R_i and R_p on the 1/6 and 1/3 powers, respectively, of the *n*-butyllithium concentration. Molecular-weight measurements by viscometry and light scattering have been used to support the presence of the monomer and dimer species, but the results from different workers are often contradictory [Van Beylen et al., 1988]. This interpretation of the fractional reaction orders is not only for monomeric initiator and propagating ion pairs are reasonable. This interpretation is not universally accepted for all reaction systems. It has been suggested that for the systems the fractional reaction orders are artifacts resulting from the complex manner in which concentration affects the reaction of monomer with associated initiator and propagating species [Young et al., 1984].

The results are slightly different with *i*- and *t*-butyllithium. R_i is still 1/3-order in initiator but R_p is 1/2 instead of 1/3-order in initiator. *i*- and *t*-butyllithium exist as dimers, not hexamers like *n*-butyllithium, because of the more sterically hindered β -hydrogen groups. The propagating species still associates as dimers. Since the monomer group becomes far removed from the propagating carbanion center, the

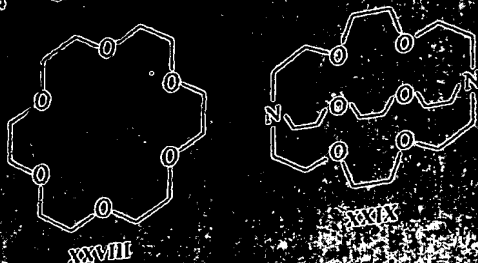
initiation by *s*- and *t*-butyllithium are greater than for *n*-butyllithium, a consequence of the greater nucleophilicity of tertiary and secondary carbanions over primary carbanions. The relative reactivities of *s*- and *t*-butyllithium are not always in the same order but depend on the monomer, indicating that steric effects are also important.

Polymerization in aliphatic hydrocarbons is considerably slower than in aromatic hydrocarbons because of decreased dissociation of initiator and propagating ion-pair aggregates. The course of reaction in aliphatic hydrocarbons is complex compared to that in aromatic solvents. Initiation is very slow at the start of reaction but proceeds with autoacceleration as *cross* or *mixed association* of initiator and propagating ion pairs replaces self-association of initiator. Cross association is weaker and results in an increased concentration of monomeric initiator. This effect may also explain the higher-order dependence of R_p on initiator (typically between $\frac{1}{2}$ - and 1-order) in aliphatic solvents, especially for *s*- and *t*-butyllithium. R_p is still $\frac{1}{2}$ -order in initiator independent of solvent.

The situation is similar qualitatively but differs quantitatively for isoprene and 1,3-butadiene. The dependence of R_p on initiator varies from $\frac{1}{2}$ - to 1-order depending on the specific reaction system. The reaction orders for all monomers are affected by the relative as well as absolute concentrations of initiator and monomer. Thus the dependence of R_p on initiator for the *n*-butyllithium polymerization of isoprene in benzene at 30°C is $\frac{1}{2}$ -order at initiator concentrations above 10^{-4} M but 1-order at initiator concentrations below 10^{-4} M [Van Beylen et al., 1988]. Higher initiator concentrations yield higher degrees of aggregation and lower kinetic orders. The excess of monomer over initiator is also important. Higher kinetic orders are often observed as the monomer: initiator ratio increases, apparently as a result of breakup of initiator and propagating ion-pair associations by monomer.

The association phenomena occurring with alkyl lithium initiators in nonpolar solvents results in very low polymerization rates. A typical styrene or isoprene polymerization by butyllithium in benzene is orders of magnitude slower compared to the corresponding sodium naphthalene polymerization. When butyllithium polymerizations are carried out in polar solvents such as tetrahydrofuran, the association of initiator and propagating species vanishes completely and the polymerizations are much more rapid. The association phenomena can also be disrupted by adding a Lewis base, which can coordinate with the initiator [Alev et al., 1980; Cheminat et al., 1979; Dumas et al., 1978; Fontanille, 1989; Muller, 1989]. Polyamines such as *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and polyethers such as tetraglyme, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, are more effective in breaking up the association than are simple ethers and amines such as diethyl ether or triethylamine. The effectiveness of a Lewis base in promoting initiation and polymerization decreases if the base: initiator ratio is too high. One observes the polymerization rate to increase with increasing $[\text{base}]/[\text{RLi}]$ and then level off at a maximum rate. With many Lewis bases, the polymerization rate decreases after reaching the maximum as $[\text{base}]/[\text{RLi}]$ is increased further [Hay et al., 1976]. Complexation of base with initiator becomes so extensive as to decrease the reactivity of initiator.

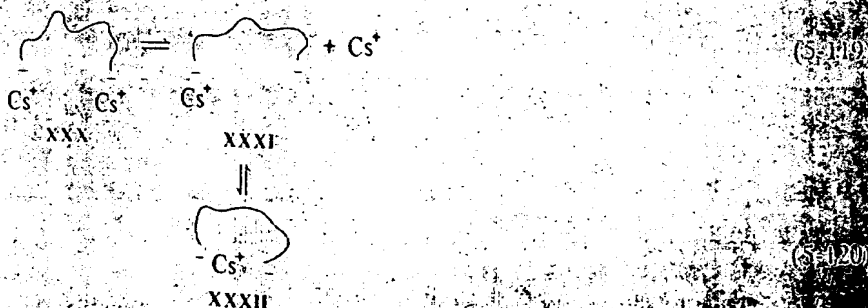
The macrocyclic crown ethers such as 18-crown-6 (XXVIII) and cryptands such as 2.2.2-cryptand (XXIX) are extremely powerful for breaking up association of organolithium compounds. These macrocyclic ligands complex lithium and also other counterions so strongly as to greatly increase the concentration of free ion propagating species, resulting in very large rate increases [Cheng and Halasa, 1976; Delfieux and Boileau, 1976].



5-3-6 Other Phenomena

The need for solvation in anionic polymerization manifests itself in some instances by other deviations from the normal reaction rate expressions. Thus the butyllithium polymerization of methyl methacrylate in toluene at -60°C shows a second-order dependence of R_p on monomer concentration [L. Abbe and Smets, 1967]. In the non-polar toluene monomer is involved in solvating the propagating species [Busson and Van Beylen, 1978]. When polymerization is carried out in the mixed solvent dioxane-toluene (a more polar solvent than toluene), the normal first-order dependence of R_p on $[M]$ is observed. The lithium diethylamide, $\text{LiN}(\text{C}_2\text{H}_5)_2$, polymerization of styrene at 25°C in THF-benzene similarly shows an increased order of dependence of R_p on $[M]$ as the amount of tetrahydrofuran is decreased [Hurley and Tait, 1976].

Propagation of two-ended (bifunctional) propagating species often proceeds at a lower rate than the corresponding monoanion species as a result of triple ion formation [Bhattacharyya et al., 1964]. For example, ionic dissociation of the counterion from one end of the cesium salt of a two-ended propagating species XXX yields XXXI, in which the newly dissociated anionic center remains near the ion-pair at the other end of XXXI. The result is XXXII, referred to as a triple ion.



The triple ion propagates faster than a simple ion pair but slower than a free ion [Muller, 1989]. The major effect of triple ion formation is a lowering of the concentration of free ions, and the overall result is a decrease in polymerization rate. Similar results are found for divalent counterions such as barium and strontium [de Groot et al., 1975, 1977; Mathis and Francois, 1978; Mathis et al., 1978]. Triple ion formation decreases with increasing molecular weight of the two-ended dianion; thus, R_p increases with conversion. As the length of the intramolecular chain between the two anion centers increases, the probability of cyclization to the triple ion decreases.

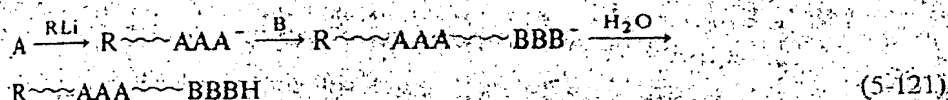
The higher reactivity of 2-vinylpyridine relative to styrene has been attributed to a combination of intramolecular solvation and triple ion formation [Sigwalt, 1975; Soum et al., 1977].

5.4 BLOCK COPOLYMERS

There has been increasing activity in synthesizing block copolymers (Sec. 2-13a) since these offer the potential for obtaining products that can incorporate the desirable properties of two or more homopolymers. There are several different approaches to synthesizing polymers with long blocks of two (or more) different monomers [Allport and James, 1973; Ceresa, 1973; Noshay and McGrath, 1977]. All the methods require considerable theoretical understanding and manipulative skills to obtain well-defined products.

5.4a Sequential Monomer Addition

Sequential addition of monomers to a living anionic polymerization system is at present the most useful method of synthesizing well-defined block copolymers [Morton, 1983; Morton and Fetters, 1977; Rempp et al., 1988]. An AB diblock copolymer is produced by polymerization of monomer A to completion using an initiator such as butyllithium. Monomer B is then added to the living polyA carbanions. When B has reacted completely a terminating agent such as water is added.



and then the AB block copolymer isolated [Fetters et al., 1978]. This method can be used to synthesize any of the various types of block copolymers (di, tri, tetra, penta, multiblocks) by employing the proper sequencing of additions of different monomers provided that each propagating carbanion can initiate the polymerization of the next monomer. For example, polystyryl carbanion will initiate polymerization of methyl methacrylate, but the reverse does not occur. Synthesis of a styrene-methyl methacrylate diblock copolymer requires that styrene be the first monomer. Further, it is useful to decrease the nucleophilicity of polystyryl carbanions by adding a small amount of 1,1-diphenylethylene to minimize attack at the ester function of methyl methacrylate (MMA). Sequencing is not a problem in synthesizing block copolymers of styrene with isoprene or 1,3-butadiene. The length of each segment in the block copolymer is determined by the amount of each monomer added relative to the amount of initiator. The overall properties of the product vary with the block lengths of the different monomers.

Difunctional initiators such as sodium naphthalene can be advantageously used to synthesize ABA, BABAB, CABAC, and other symmetrical block copolymers [Benson et al., 1985; Foss et al., 1977] more efficiently, that is, using fewer cycles of monomer additions. Difunctional initiators can also be prepared by reacting a diene (e.g., *m*-diisopropenylbenzene, 1,3-bis[1-phenylvinyl]benzene) with two equivalents of *s*- or *t*-butyllithium. Monomer B is initiated by a difunctional initiator followed by monomer A. A polymerizes at both ends of the B block to form an ABA triblock. BABAB

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